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THE REMOVAL OF ALKALI METALS FROM A MAGNETITE CONCENTRATE BY ADDITIVES

by

J. Wilson

ABSTRACT

Volatilization tests show that a silica/alkali ratio at 100/1 may be attained in a magnetite concentrate by firing it for five minutes at 1300°C in air with the addition of $CaCl_2$, NH_4Cl or $MgCl_2$ salt. The salt dosage rate required may be either 0.12 or 0.06 % by wt with a basicity index of 0.14 or 0.23 respectively.

ÉLIMINATION DES MÉTAUX ALCALINS D'UN CONCENTRÉ DE MAGNÉTITE À L'AIDE D'ADDITIFS

par

J. Wilson

RÉSUMÉ

Des essais de volatisation ont démontré que l'on peut obtenir un rapport siliceux/alcali de 100/1 d'un concentré de magnétite en le chauffant à l'air à 1300°C pendant 5 minutes en ajoutant du $CaCl_2$ et du sel de NH_4CL ou de $MgCl_2$. La quantité de sel nécessaire peut être de 0,12 ou 0,06 % massique avec un indice de basicité de ,14 ou ,23 respectivement.

INTRODUCTION

A common feature of most northern Ontario iron ore deposits is the presence of appreciable amounts of alkali-bearing gangue minerals. These minerals normally comprise the alkali feldspars, mica, sericite, riebeckite and stilpnomelene. Although mineral beneficiation removes most of these minerals, minute amounts still remain in the concentrate. It is these minute amounts that, if allowed to build up, can cause serious operational problems in the blast furnace. The alkalis attack the burden causing degradation of the coke and swelling and disintegration of the pellets. This leads to non-uniform burden permeability associated with channeling of the blast, higher blast pressures, erratic burden movement and chilled hearths. Alkalis also attack furnace linings causing accretions or scaffolds to form which further reduce burden permeability, furnace volume and brick life (1). Although most excess alkali levels in the feed can be handled in the blast furnace by adjusting operating conditions, clearly a better solution is to remove the alkalis before they are charged.

The near total removal of alkali minerals is possible by present ore dressing methods but due to their intimate association with quartz and/or magnetite the concurrent loss of iron and/or silica would be unacceptably high. Present blast furnace practice requires a 3 to 5% silica level. Further liberation is undesireable because of the production of excess slimes and the increased grinding costs.

A possible alternate route in which the alkali is removed by volatilization with chlorine or chlorine-bearing salts at high temperature is worth investigating (2,3).

The Kowa-Seiko Process uses $CaCl_2$ to remove deleterious metals from pellets of pyrite cinder using a rotary kiln (4). Similarly the CV (or LDK) process uses chlorine gas to remove impurities from pyrite cinders in a special shaft furnace (5). The implementation of a chloridizing process in iron ore pelletizing would be relatively simple because no special equipment would be required other than adding a chloride salt solution along with the balling water at the balling drum. The salt may even improve the physical properties of the green, dry and fired pellets thereby allowing a reduction in bentonite consumption and possibly induration temperature (6). Although the successful commercial application of chloride salts in iron ore pelletizing has never been reported in the

literature the laboratory results of Lapkowsky and Lu (7) using an iron ore tailing and granite rock are encouraging.

EXPERIMENTAL METHOD

The as-received magnetite flotation concentrate was characterized by chemical assay and mineralogical examination for the important size fractions (see Tables 1 and 2).

TABLE 1

Chemical analysis of magnetite concentrate by size fraction

Size Fraction	Wt %	Tot Fe %	Sol Fe %	Na_2O %	SiO_2 %	K_2O %	CaO	MgO	Al_2O_3
Head	100.0	69.53	68.91	.047	3.03	.057	.12	.12	.39
+200 M	0.4	*	*	.14	10.74	.16	-	-	-
-200 +270 M	5.6	64.89	64.79	.11	8.67	.12	-	-	-
-270 +400 M	13.6	68.70	68.29	.06	3.91	.07	-	-	-
-400 +500 M	23.3	69.84	69.32	.04	2.75	.06	-	-	-
-500 M	57.1	70.25	69.94	.03	1.90	.05	-	-	-

*Insufficient sample

TABLE 2

Mineralogical analysis of magnetite concentrate by size fraction

Mineral	Head	+200 M	-200 +270 M	-270 +400 M	-400 +500 M	-500 M
Magnetite-free	86.3	79.0	77.3	91.1	93.9	92.7
unliberated	4.3	9.6	10.7	2.7	1.8	1.2
Hematite	0.4	0.2	0.4	0.1	0.1	0.3
Quartz	8.5	8.1	8.4	3.7	3.4	5.3
K-spar + phlogopite	.08	2.7*	0.7	1.0	0.4	0.1
Phlogopite	na	na	0.4	na	0.3	na
K-spar	na	na	0.3	na	0.1	na
Plagioclase	nd	nd	0.8	0.3	0.2	.02
Mafics	0.4	0.4	1.4	1.1	0.2	0.4

na not analyzed
nd not detected
* mostly K-spar

During preliminary testwork the following additives were tried: NH_4HF_2, NH_4HSO_4, Na_2CO_3, NaOH, $FeCl_2$, $FeCl_3$, $BaCl_2$, $CaCl_2$, NH_4Cl and $MgCl_2$.

The chloride salts proved superior and so $FeCl_3$, $CaCl_2$, NH_4Cl and $MgCl_2$ were selected for further study. The experimental parameters chosen for the tests were basicity, salt dosage, peak induration temperature and time at peak induration temperature. Both alundum and nickel crucibles were tried with no appreciable difference in the results.

To obtain more consistent results the salts were added to the concentrate as a solution of known concentration. The amounts of salts added were 0.6 and 1.2 stoichiometric requirements, one stoichiometric requirement (or equivalent) being the amount of salt that satisfies both equations:

$$2Cl^- + K_2O \longrightarrow 2KCl + O^=$$

$$2Cl^- + Na_2O \longrightarrow 2NaCl + O^=$$

After drying overnight at 105°C the powder was mixed thoroughly by hand to ensure homogeneity and then split into 20 g samples for the firing step. At this point the final basicity was adjusted by adding reagent grade CaO. Three levels of basicity were used, .09, .14 and .23 where

$$\text{Basicity} = \frac{\% \text{ CaO} + \% \text{ MgO}}{\% \text{ SiO}_2 + \% \text{ Al}_2\text{O}_3}$$

A vertical tubular Lindberg electric furnace capable of a temperature of 1500°C was used for firing. The samples were introduced from below and raised into the hot zone by a screw mechanism at a rate that produced a heat cycle consistent with normal industrial practice (see Fig. 1). Three levels of peak temperature were investigated, 1250, 1300 and 1350°C. These were maintained for five minutes. To investigate time as a factor some extra runs were done for ten and twenty minutes. After the firing cycle was completed the sample was cooled and ground to 100% -80 μm and assayed. All assays were done by wet chemical analysis. Repeats were performed on several runs to determine experimental error and final basicities were checked randomly.

RESULTS

Assaying was done for K_2O, Na_2O and SiO_2 on every sample and for total iron, CaO, MgO, Al_2O_3 randomly. A statistical analysis of the results showed a good correlation between alkali removal versus basicity and salt concentration. Temperature and time showed poor correlation. Per cent alkali loss and final alkali ratio (SiO_2/alkali) are plotted against final basicity for each salt and dosage level (see Figures 2-9). Each point on the graphs represents the average of the results for all three temperatures 1250, 1300 and 1350°C. Graphs of per cent alkali loss versus time at peak temperature for all the salts are also shown (see Figures 10-13). The effect of peak temperature on alkali removal was insignificant so those results are not shown.

Reproducibility of the results is shown in Table 3 and a comparison of expected and actual final basicities is shown in Table 4.

TABLE 3

Typical reproducibility for selected repeats

Run No.	Salt	Equiv.	Basicity	Temp. °C	% K_2O Loss	% Na_2O Loss
40	$FeCl_3$	1.2	.09	1250	24	19
103	$FeCl_3$	1.2	.09	1250	19	19
43	$FeCl_3$	.6	.09	1350	24	21
95	$FeCl_3$	.6	.09	1350	22	14
44	$FeCl_3$	.6	.14	1350	26	21
96	$FeCl_3$	.6	.14	1350	28	27
53	$FeCl_3$	1.2	.14	1300	46	25
55	$FeCl_3$	1.2	.14	1300	53	30
18	$CaCl_2$	1.2	.23	1300	60	34
89	$CaCl_2$	1.2	.23	1300	53	38
22	NH_4Cl	1.2	.09	1250	37	14
93	NH_4Cl	1.2	.09	1250	46	30

TABLE 4

A comparison of expected and actual basicities for selected runs

Run No.	Expected Basicity	Actual Basicity
13	.09	.10
14	.14	.10
31	.09	.08
32	.14	.12
49	.09	.08
51	.23	.21
68	.09	.09
76	.23	.24
116	.23	.18

OBSERVATIONS AND DISCUSSION

The following observations may be made for the range of experimental conditions.

1. Alkali removal is related to basicity. The correlation is stronger for K_2O than for Na_2O.

2. Alkali removal is related to salt dosage.

3. Peak reaction temperature has no significant effect on alkali removal.

4. The time at peak reaction temperature had little effect on K_2O removal and therefore a reaction time of five minutes appears sufficient. For Na_2O, however, 10 minutes are required to complete its removal.

5. The relative effectiveness of the various chloride salts are, in descending order:
   For K_2O removal:

$$NH_4Cl \geq MgCl_2 \geq CaCl_2 \geq FeCl_3$$

where NH_4Cl is significantly better than either $CaCl_2$ or $FeCl_3$.
For Na_2O removal

$$FeCl_3 \geq MgCl_2 \geq CaCl_2 \geq NH_4Cl$$

where $FeCl_3$ is significantly better than NH_4Cl.

The switch in the relative position of NH_4Cl and $FeCl_3$ for K_2O versus Na_2O is interesting.

6. On the average, K_2O removal is 100% higher than Na_2O removal for all the salts for a reaction time of 5 minutes.

7. Iron and silica losses were not detected.

8. The assumption of final basicity proved to be valid, which means that aside from the alkalis there was no loss of material.

9. The repeatability of the results for alkali loss was not good, as is shown in Table 3. This is due to the large relative error associated with measuring the minute quantities of total alkali present in the concentrate. However, it is the author's opinion that the averaged results, as shown in Figures 3-13, show the true relationships between alkali removal and the experimental parameters studied.

CONCLUSIONS

For all the salts tested except $FeCl_3$ the optimum conditions required for removing enough alkali to approximate an alkali ratio of 100:1 (SiO_2/K_2O) are:

a) 5 minutes at 1300°C, dosage = 0.6 equivalents, basicity = 0.23.

b) 5 minutes at 1300°C, dosage = 1.2 equivalents, basicity = 0.14.

where 1 equivalent of salt ≈ 0.1% of the sample by weight.

RECOMMENDATIONS

It is acknowledged that aside from lime the additives investigated here are relatively expensive. Therefore it would be of interest to investigate alkali removal rates at much higher basicities (up to 1.0) to see if the 100/1 ratio can be maintained at a lower salt rate. The possible future production of fluxed pellets may have a positive effect on alkali removal using chloride salts.

Other possible work should include an investigation of the properties of green balls and fired pellets produced with the salts, the possible concurrent reduction in bentonite rate and the use of combinations of salts.

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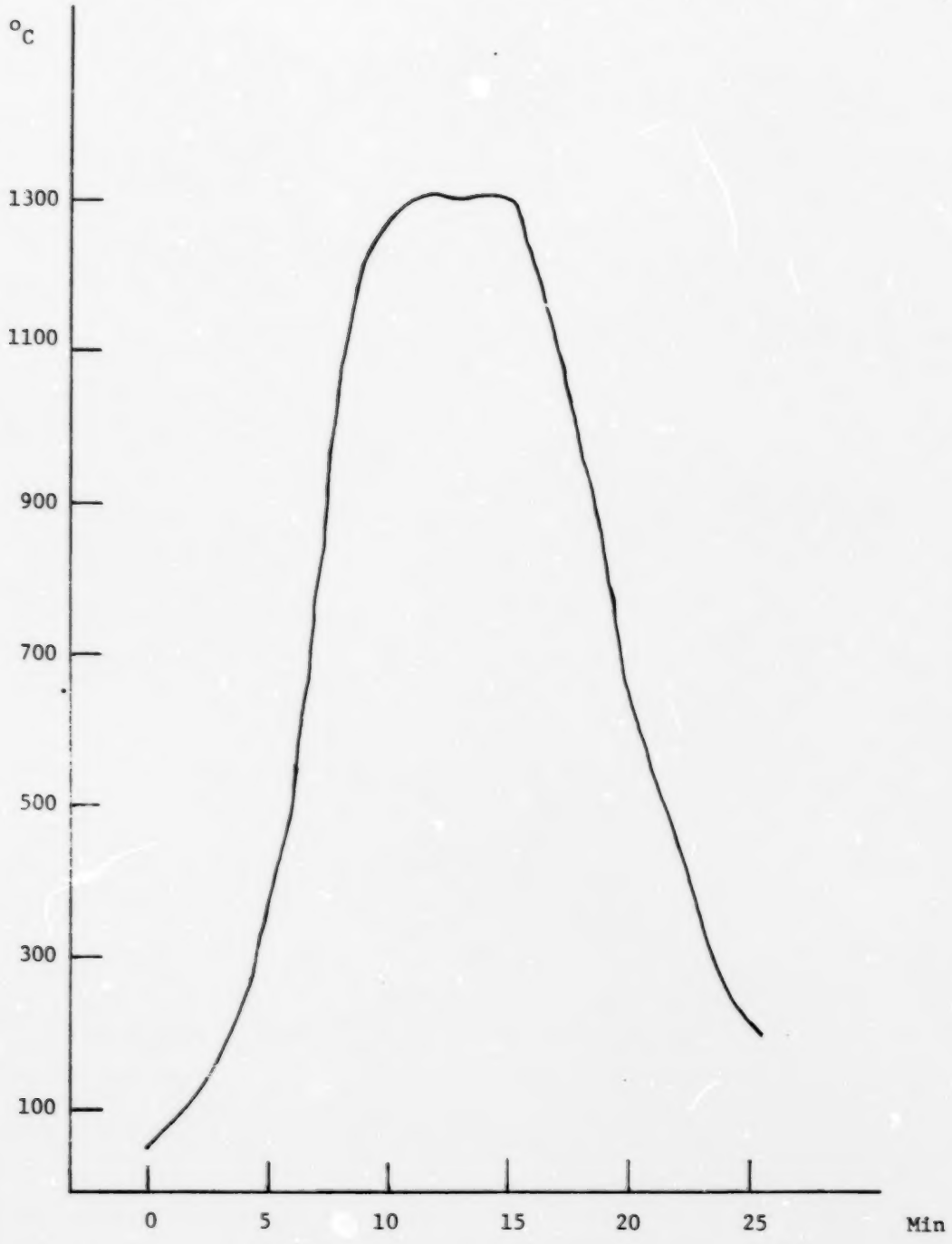

Fig. 1 - A typical heat cycle for firing concentrate at 1300°C for five minutes.

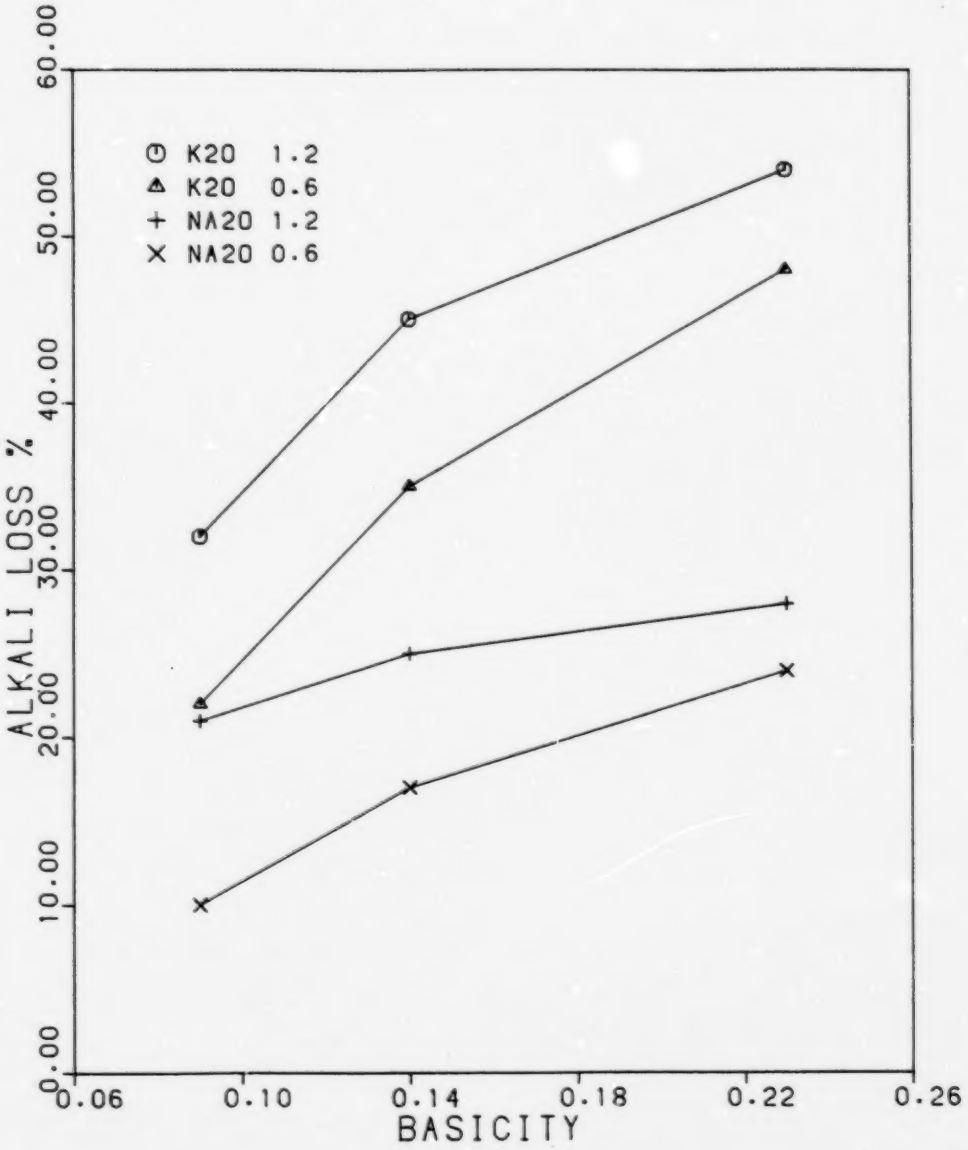

Fig. 2. Alkali loss vs basicity for calcl 2.

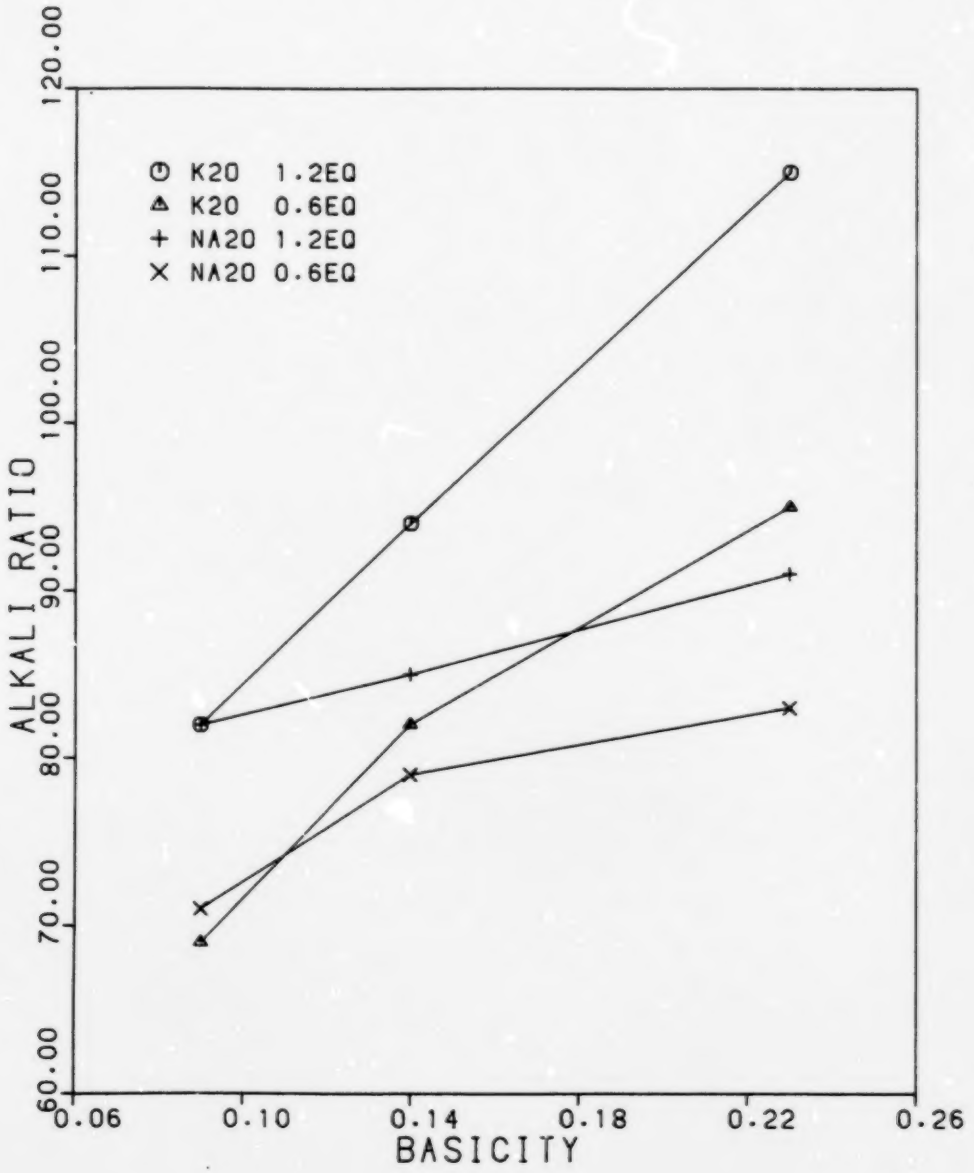

Fig. 3. Alkali ratio vs basicity for calcl 2.

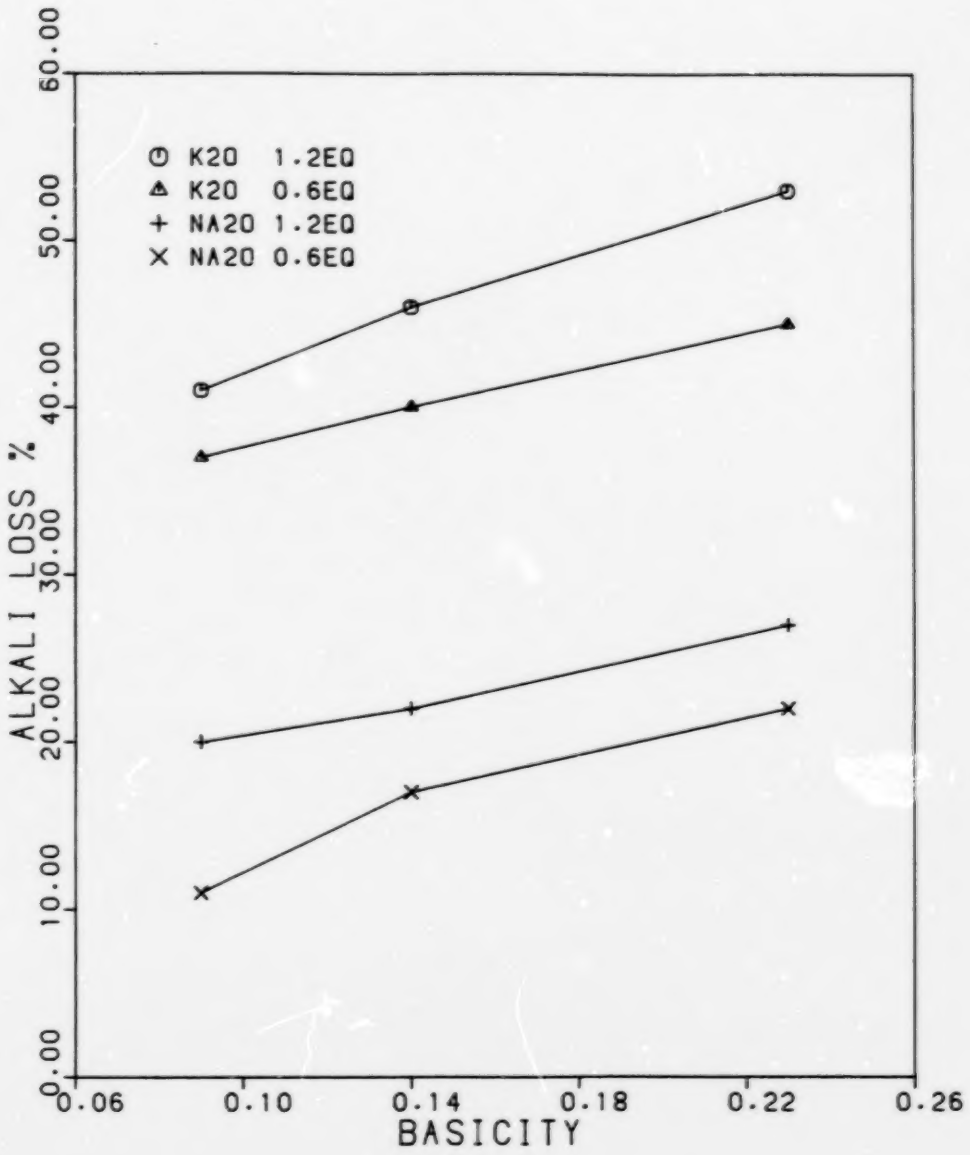

Fig. 4. Alkali loss vs basicity for NH4CL.

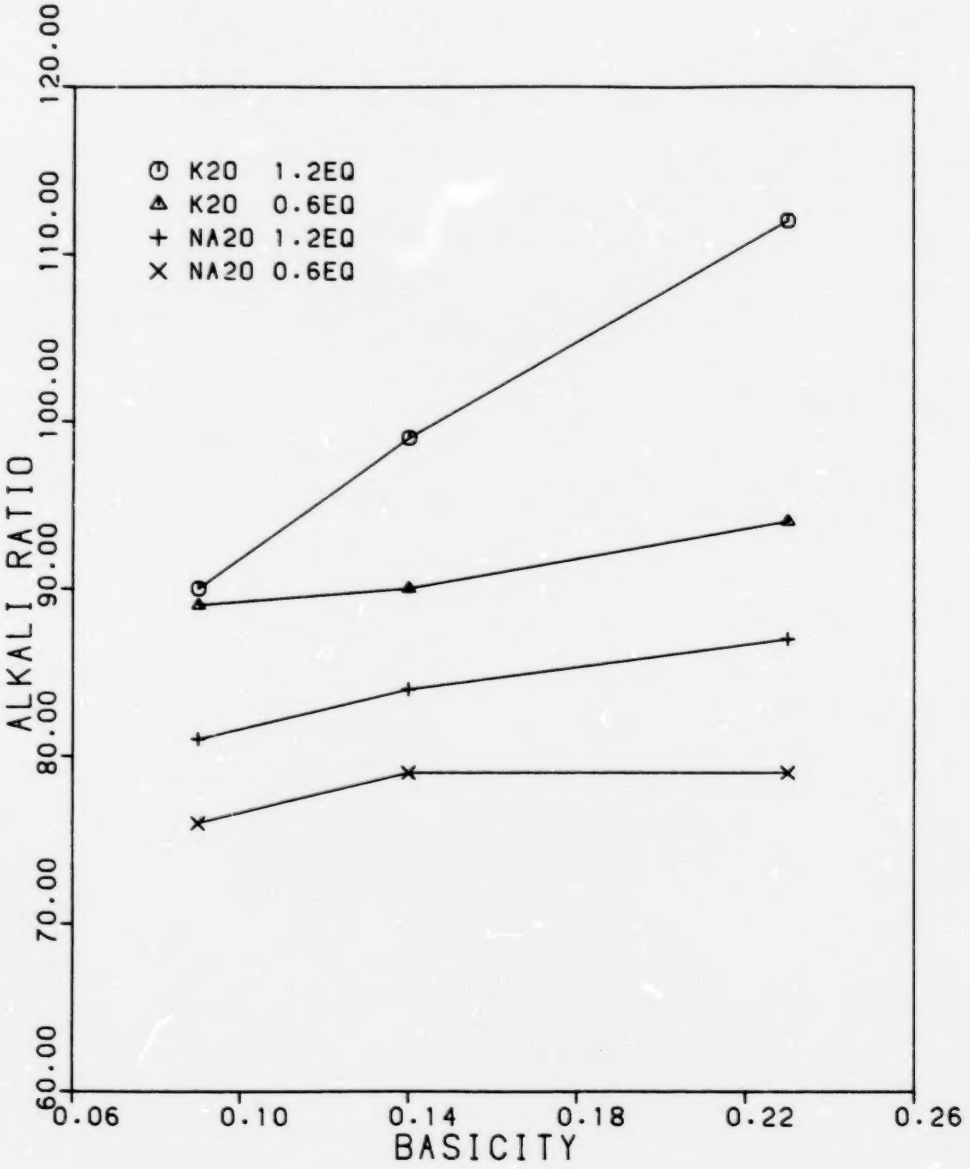

Fig. 5. Alkali ratio vs basicity for NH4CL.

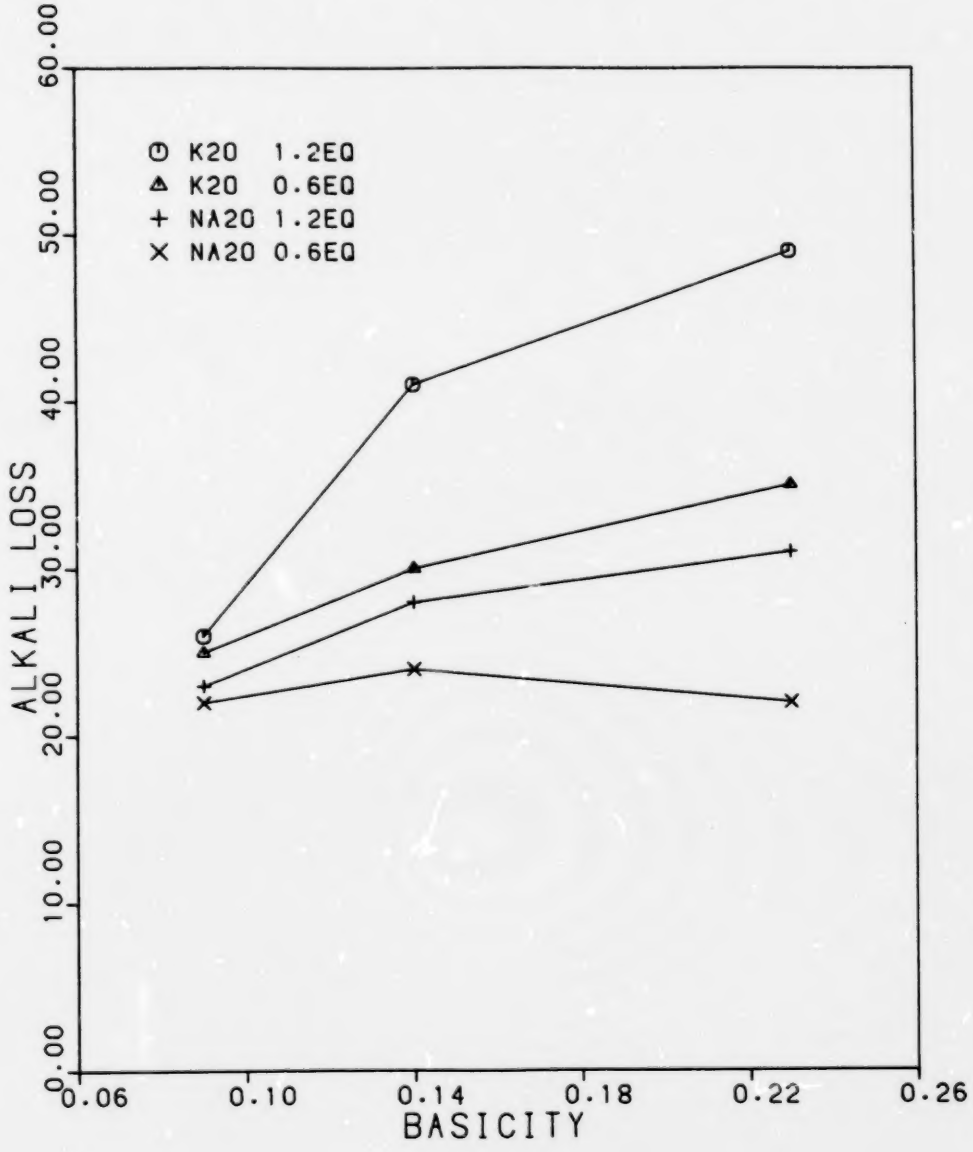

Fig. 6. Alkali loss vs basicity for FECL3.

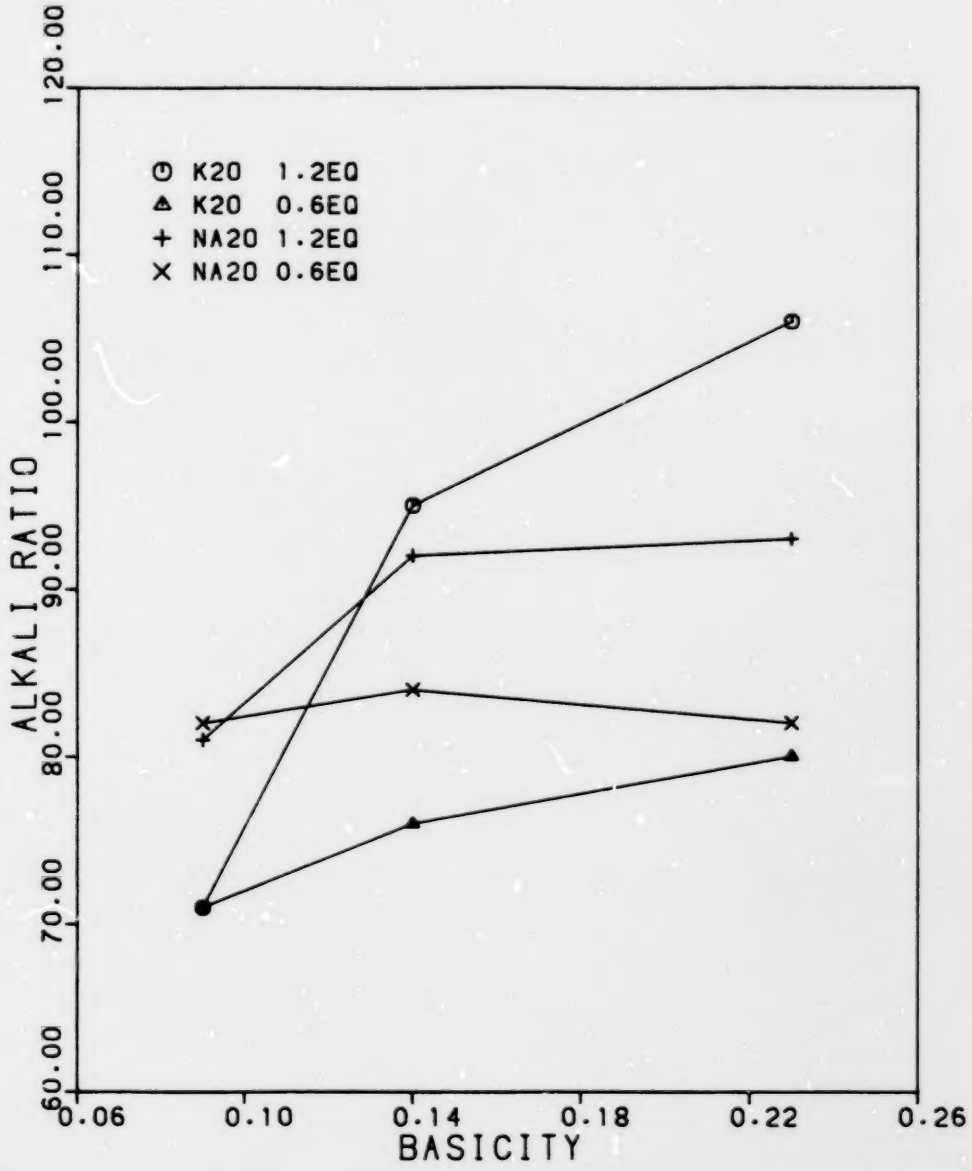

Fig. 7. Alkali ratio vs basicity for FECL3.

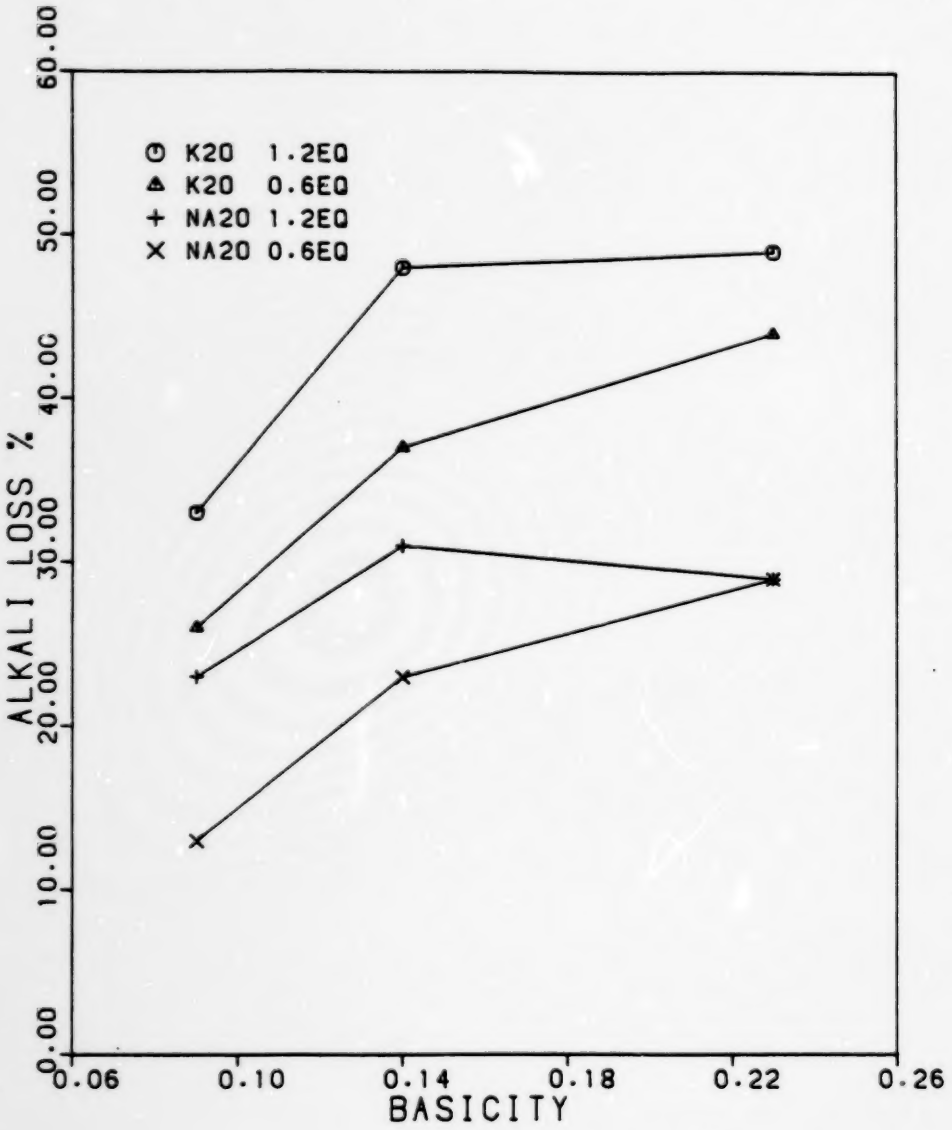

Fig. 8. Alkali loss vs basicity for MGCL2.

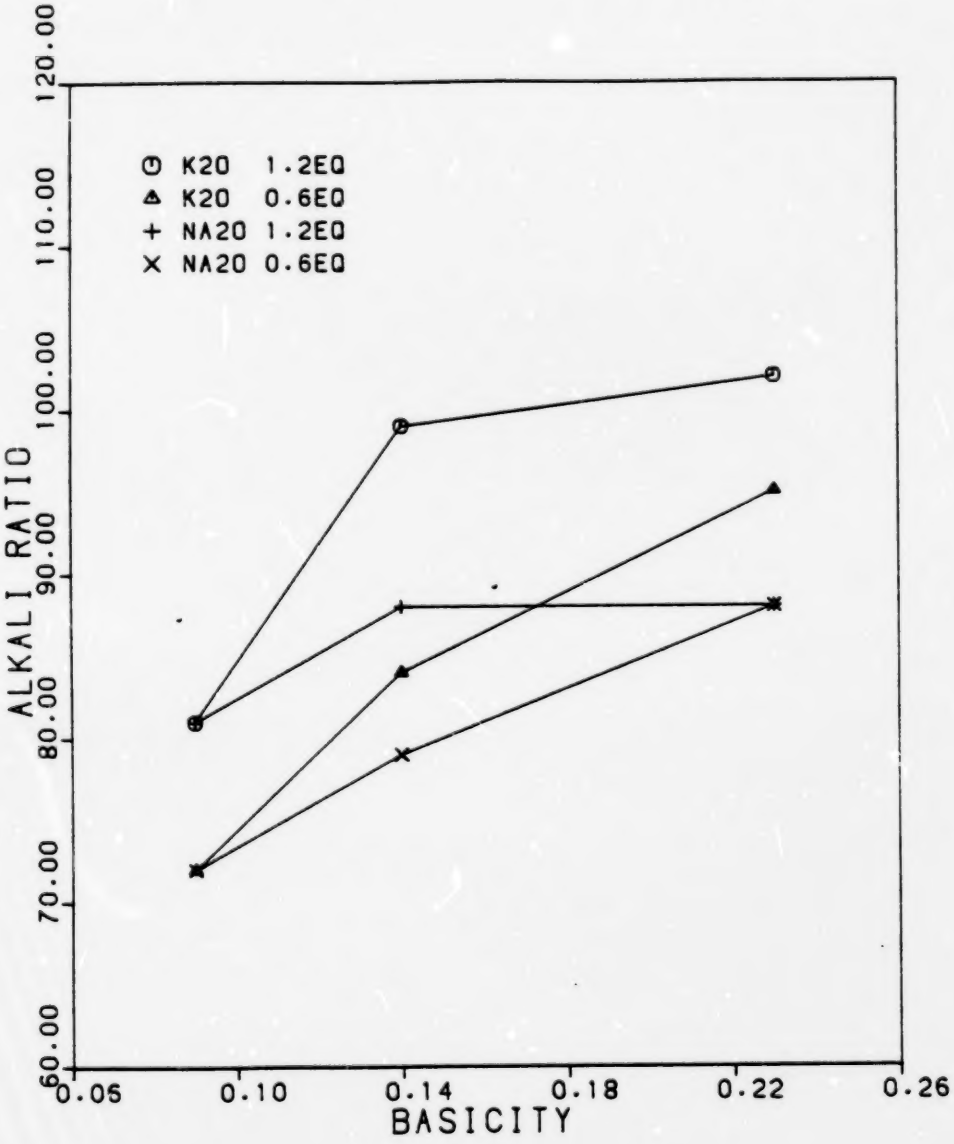

Fig. 9. Alkali ratio vs basicity for MGCL2.

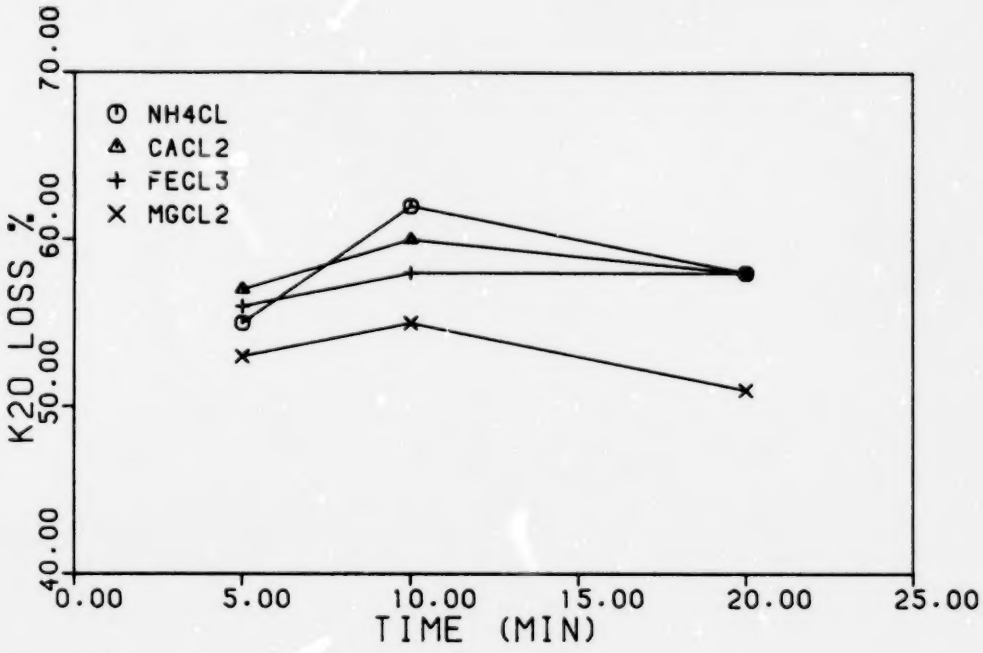

Fig. 10. K20 loss vs time.
(Dosage = 12 EQ, Basicity = 23, temp. = 1300°C)

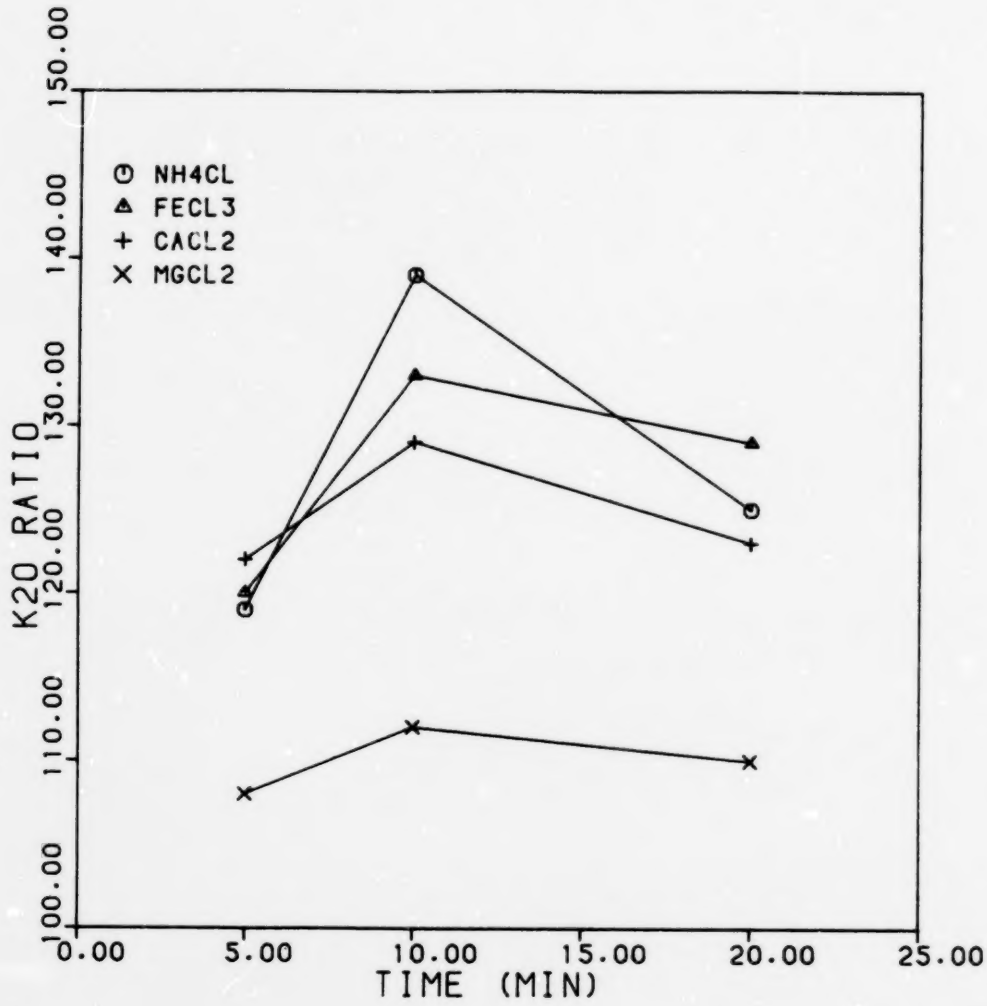

Fig. 11. K20 ratio vs time.
(Dosage = 1.2 EQ, Basicity = 23, Temp. = 1300°C)

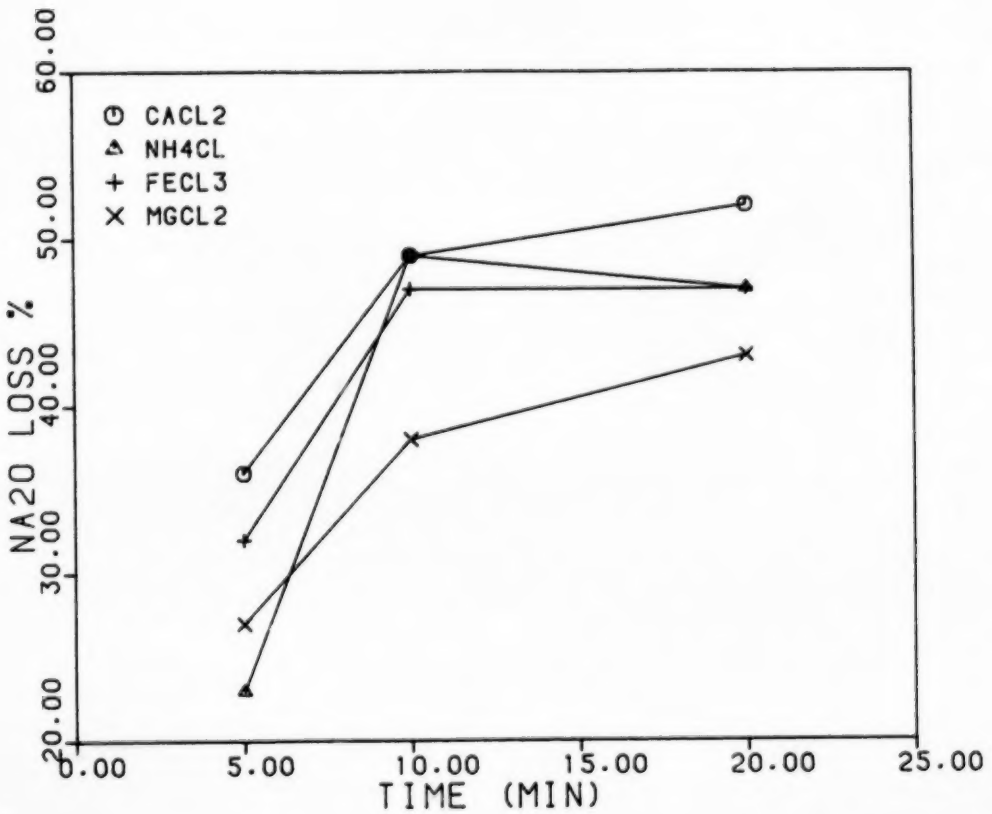

Fig. 12. NA2O loss vs time.
(Dosage = 1.2 EQ, Basicity = 23, Temp. = 1300°C)

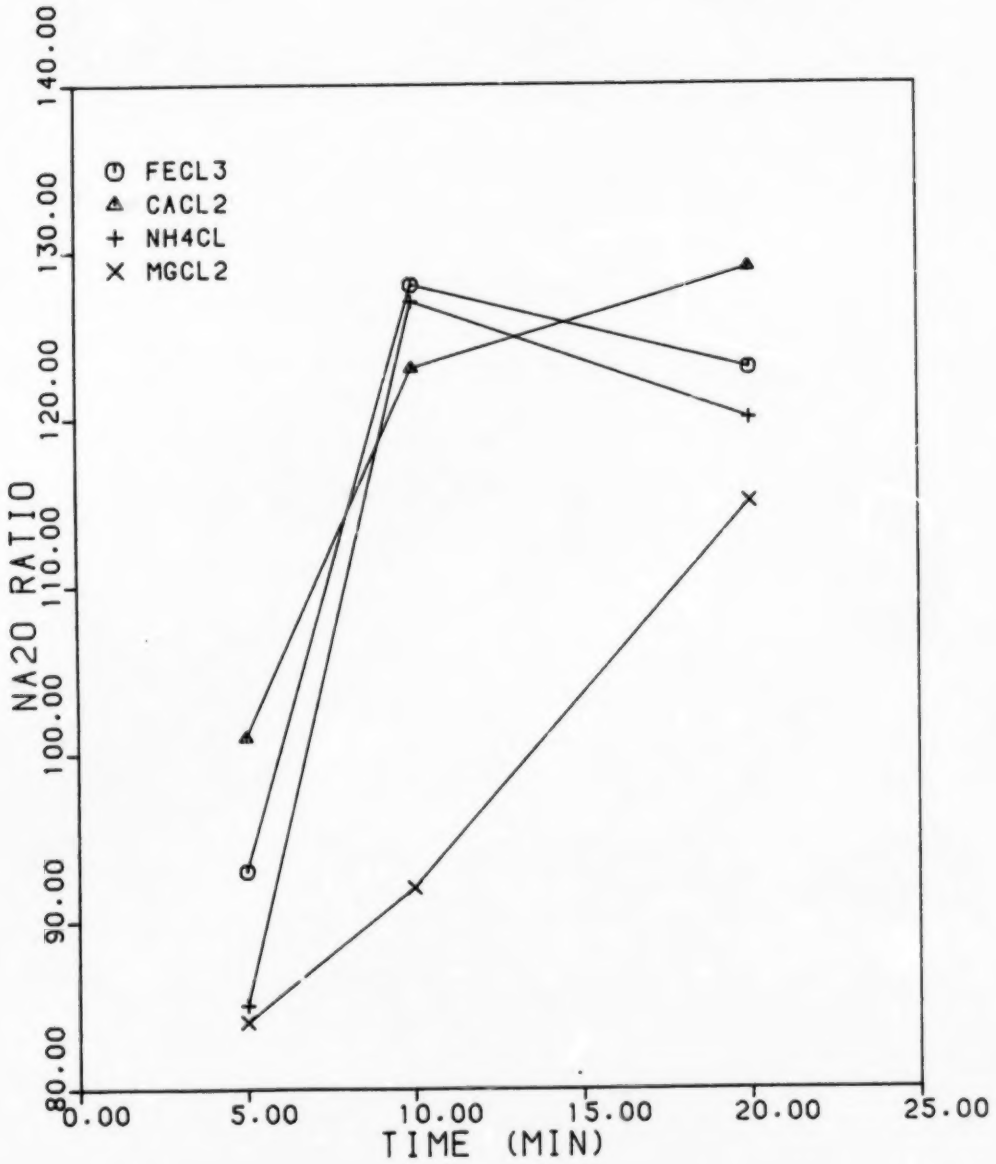

Fig. 13. NA2O ratio vs time.
(Dosage = 1.2 EQ, Basicity = 23, Temp. = 1300°C)